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(54) Title: GOLF BALL INCORPORATING METALLOCENE POLYMER BLENDS (57) Abstract The disclosed invention provides novel golf ball compositions which contain olefinic based ionomers and non-ionic olefinic copolymers produced by use of metallocene catalysts. These compositions exhibit improved mechanical properties such as tensile and flexural properties, and can be foamed or unfoamed. Golf balls that employ at least one layer of these blends in any of the golf ball cover, core, or a mantle situated between the cover and the core provide ball properties and performance similar to and in some cases better than the state of the art ionomer based golf balls.		

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GOLF BALL INCORPORATING METALLOCENE POLYMER BLENDS

This application is a continuation-in-part of U.S. application Serial No. 08/482,514, filed on June 7, 1995, which is a continuation-in-part of U.S. application Serial No. 08/377,553 filed January 24, 1995 (now abandoned).

FIELD OF THE INVENTION

The present invention relates to golf balls and, in particular, to golf balls having at least one layer comprising at least one polyolefin polymer produced using a single-site metallocene catalyst in the polymerization process. The metallocene polymer may be mixed with an ionomer to form a blend, and may be foamed or unfoamed. The layer may be located in any of the cover or core of the ball or in a mantle layer located between the cover and the core.

BACKGROUND OF THE INVENTION

Three-piece, wound golf balls with balata covers are preferred by most expert golfers. These balls provide a combination of distance, high spin rate, and control that is not available with other types of golf balls. However, balata is easily damaged in normal play, and, thus, lacks the durability required by the average golfer.

In contrast, amateur golfers typically prefer a solid, two-piece ball with an ionomer cover, which provides a combination of distance and durability. Because of the hard ionomer cover, these balls are almost impossible to cut, but also have a very hard "feel", which may golfers find unacceptable, and a lower spin rate, making these balls more difficult to draw or fade. The differences in the spin rate can be attributed to the differences in the composition and construction of both the cover and the core.

Many attempts have been made to produce a golf ball with the control and feel of a wound balata ball and the durability of a solid, two-piece ball, but none have succeeded totally. For example, U.S. Patent No. 4,274,637 to

Molitor discloses two- and three-piece golf balls having covers completely or partially formed from a cellular polymeric material to improve backspin, but does not provide any examples that compare the spin rates of the disclosed 5 golf balls with those of prior art balls.

U.S. Patent No. 5,002,281 to Nakahara et al. discloses a three-piece solid golf ball having an ionomer cover and a solid core consisting of a soft inner core and a hard outer shell, where the difference in the hardness of the 10 two parts of the core is at least 10 on the JIS-C scale.

Similarly, U.S. Patent No. 4,781,383 discloses a solid, three-piece golf ball, having an ionomer cover and a core with inner and outer layers, where the inner layer has a diameter of 24 to 29 mm and a Shore D hardness of 15 to 30, 15 and the outer layer has a diameter of 36 to 41 and a Shore D hardness of 55 to 65. The percentage of the ball surface which contacts the club face when the ball is struck is 27 to 35 %.

European Patent Application 0 633 043 discloses a 20 solid, three-piece golf ball with an ionomer or balata cover, a center core, and an intermediate layer. The center core has a diameter of at least 29 mm and a specific gravity of less than 1.4. The intermediate layer has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a 25 hardness of at least 85 on the JIS-C scale.

Copending application no. 08/482,518 employs compressible materials, i.e., gases, in the core of a solid construction golf ball to simulate the effects of trapped air in a wound ball.

30 None of these disclosures utilizes the unique physical properties of metallocene polymers, i.e., polymers produced using single-site metallocene catalysts, which produce polymers with a narrow molecular weight distribution and uniform molecular architecture. That is, metallocene 35 catalysts provide polymers in which the order and orientation of the monomers in the polymer, and the amount and type of branching is essentially the same in each polymer chain.

The narrow molecular weight distribution and uniform molecular architecture provides metallocene polymers with properties that are not available with conventional polymers, and allow polymers to be produced having unique properties that are specifically tailored to a particular application. The desired molecular weight distribution and the molecular architecture are obtained by the selection of the appropriate metallocene catalyst and polymerization conditions. Moreover, foamed polyolefin metallocene polymers, which can be thermoformed, and provide the physical properties of rubber with the fabrication ease of polyethylene, recently became available commercially. There is no known prior art disclosure of the use of metallocene polymers in golf balls.

In addition, while different blend combinations of species of one variety of polymer, such as ionomers, have been successfully used in the prior art, different polymers, such as ionomers and balata or other non-ionic polymers have not been successfully blended for use in golf ball covers. In general, prior art blends of polymer components are immiscible or incompatible unless strong interactions are present between the polymer components in the mixture, such as those observed between ionomers and polymers containing carboxylic acid groups. In particular, this lack of compatibility exists when an ionomer is blended with a polyolefin homopolymer, copolymer, or terpolymer that does not contain ionic, acidic, basic, or other polar pendant groups, and is not produced with a metallocene catalyst. These mixtures often have poor tensile strength, impact strength, and the like. Hence, the golf balls produced from these incompatible mixtures will have inferior golf ball properties such as poor durability, cut resistance, and so on.

In this regard, U.S. Patent No. 5,397,840 discloses golf ball covers including a blend of "ionic copolymers" and "non-ionic copolymers". However, the "ionic copolymers" are defined as copolymers of an α -olefin and a metal salt of an

$\alpha\beta$ -unsaturated carboxylic acid, and the "non-ionic copolymers" are copolymers or terpolymers containing ethylene or propylene and acrylic or methacrylic acid monomers.

Therefore, strong interactions exist between the metal salts of the "ionic copolymers" and the acrylic or methacrylic acid monomers of the "non-ionic copolymers" that allow compatible blends to be formed. These interactions do not exist in prior art blends of ionomers and polymers that are truly non-ionic or nonpolar, in particular, those polymers produced with a process that does not involve the use of a metallocene catalyst.

Therefore, there is a need in the golf ball art for a golf ball incorporating metallocene polymers and blends of metallocene polymers and other polymers, such as ionomers, and in particular, foamed metallocene polymers in golf balls. The inclusion of foamed and unfoamed metallocene polymers and metallocene polymer blends will allow highly durable golf balls to be produced with virtually any combination of feel and spin rate.

20

SUMMARY OF THE INVENTION

The present invention relates to golf balls, and, in particular, to golf balls having at least one layer formed of a metallocene polymer blend, comprising from about 1 to about 100 phr of at least one metallocene polymer and from about 99 to 0 phr of at least one ionomer. The layer may form at least a portion of any of the cover, core or mantle of the golf ball, where the mantle is situated between the cover and the core. Any of the core, cover, and mantle of the golf balls of the invention can be formed of one layer or a plurality of layers, as that term is defined herein. In the preferred embodiment, the layer has a foamed structure. Generally, the metallocene polymer has a flexural modulus of from about 500 psi to 200,000 psi, and the ionomer has a flexural modulus of from about 50 psi to about 150,000 psi. For a metallocene polymer blend having a foamed structure,

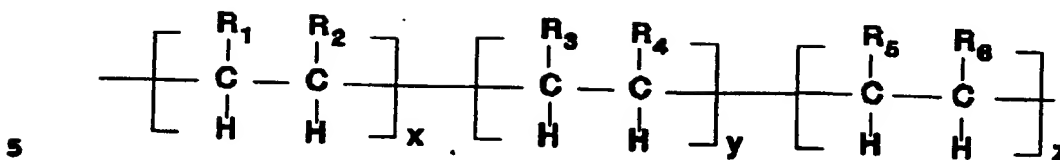
the preferred flexural modulus ranges from about 1000 to 150,000 psi.

For golf ball covers having a layer of metallocene polymer blend with a foamed structure, the layer preferably has a Shore D hardness of from about 15 to about 80 and a thickness of from about 0.005 to 0.125 inch.

Generally, for golf ball cores having a layer of metallocene polymer blend with a foamed structure, the layer generally has a Shore D hardness of from about 15 to about 80 and a thickness of from about 0.005 to 0.125 inch. The core preferably has a diameter of from about 1 to 1.63 inch. Where the metallocene polymer blend layer is situated in an outer portion of the core, the core may comprises a liquid center or a solid polymeric center.

For golf balls comprising a cover and a core and a mantle situated between the cover and the core, where the mantle has a layer of metallocene polymer blend layer with a foamed structure, the layer preferably has a Shore D hardness of from about 15 to about 80 and a thickness of from about 0.005 to 0.125 inch. Cores in golf balls according to the invention for use with mantles may comprise a liquid or solid center wrapped in elastomeric windings. Preferably, in golf balls with such mantles, the core has a diameter of from about 1 to 1.63 inch and the cover has a thickness of from about 0.005 to 0.125 inch.

Preferably, the metallocene polymer is polyethylene or a copolymers of ethylene with butene, hexene, octene, or norbornene. Pendant groups may be also added to metallocene polymers by post-polymerization reactions to modify physical or chemical properties of the polymer. Metallocene polymers useful with the golf balls of the invention include metallocene polymers of the formula:



wherein

R_1 is hydrogen;

10 R_2 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

R_3 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

R_4 is selected from the group consisting of H, CH_3 , C_2H_5 , C_3H_7 ,
15 C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , C_9H_{19} , $C_{10}H_{21}$, and phenyl, in which from 0 to 5 H within R_4 can be replaced by substituents selected from the group consisting of $COOH$, SO_3H , NH_2 , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that R_3 and R_4 can be combined to

20 form a bicyclic ring;

R_5 is hydrogen, lower alkyl including C_1-C_5 , carbocyclic, aromatic or heterocyclic;

R_6 is hydrogen, lower alkyl including C_1-C_5 , carbocyclic, aromatic or heterocyclic; and

25 wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer and z ranges from 0 to 49 weight per cent of the polymer.

The use of foamed metallocene polymer also allows the golf ball designer to adjust the density or mass
30 distribution of the ball to adjust the angular moment of inertia, and, thus, the spin rate and performance of the ball. Foamed materials also offer a potential cost savings due to the reduced use of polymeric material. Where at least a portion of the core is formed from a foamed metallocene
35 polymer blend, a density increasing filler material can be added to the cover or the mantle to distribute the mass of

the ball towards the outer surface and increase the angular moment of inertia. Similarly, where the layer forms at least a portion of the cover, the density increasing filler material can be added to the core to decrease the angular
5 moment of inertia. Alternatively, where the layer forms at least a portion of the mantle, a density increasing filler material can be added to either the cover or the core.

Preferably, a golf ball according to the invention comprises a cover and a core and a mantle situated between
10 the cover and the core, wherein at least one of the cover, the core, and the mantle comprises at least one layer comprising a metallocene polymer blend, and the metallocene polymer blend comprises from about 1 to about 100 phr of at least one metallocene polymer, such as those described above,
15 and from about 99 to 0 phr of at least one ionomer. Most preferably, the layer has a foamed structure, and the layer forms at least a portion of the mantle.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Fig. 1 is a cross-sectional view of a two-piece golf ball according to the invention with a one-piece core.

Fig. 2 is a cross-sectional view of a two-piece golf ball according to the invention incorporating a multi-layer core.

25 Fig. 3 is a cross-sectional view of a golf ball according to the invention incorporating a mantle layer between the cover and the core.

DETAILED DESCRIPTION OF THE INVENTION

30 As used herein, the term "metallocene polymer" includes any polymer, copolymer, or terpolymer, and, in particular, any polyolefin, formed using a metallocene catalyst. The term "metallocene polymer blend" includes polymer blends in which the portion of metallocene polymer
35 can range from about 1 to 100 phr (parts per hundred), based on 100 parts polymer in the blend. In addition, the term "layer" includes any generally spherical portion of a golf

ball or golf ball core, center, or mantle, including one-piece cores and one-piece balls. A mantle is defined herein as a portion of the golf ball that occupies the volume between the cover and the core. Of course, as one of ordinary skill in the art would recognize, any of the core, cover, and mantle of the golf balls of the invention can be formed of one layer or a plurality of layers, as that term is defined herein.

The present invention relates to golf balls including at least one layer comprising one or more metallocene polymers, which may be blended with at least one ionomer. The metallocene polymer blends of the invention typically comprise a compatible blend of about 1 to 100 phr of at least one metallocene polymer and about 99 to 0 phr of at least one ionomer. The blends may be foamed during molding by any conventional foaming or blowing agent. In addition, foamed metallocene polymers may be thermoformed, and, thus can be compression molded. Therefore, either injection molding or compression molding may be used to form a layer of foamed metallocene polymer in the cover, core, or mantle of a golf ball according to the invention. Metallocene polymers and metallocene polymer blends are resilient, easily processed materials that are less expensive than ionomers, and allow highly durable golf balls to be produced with virtually any combination of feel and spin rate.

Golf balls according to the invention may incorporate cores comprising metallocene polymer blends or conventional materials. Metallocene polymer blend cores may be either one-piece, comprising a single piece of foamed or unfoamed metallocene polymer blend, or multi-piece, comprising a liquid or solid core or center and one or more layers in which any of the center or the layers may comprise a foamed or unfoamed metallocene polymer blend.

For example, Fig. 1 illustrates a golf ball according to the invention with a one-piece core. Golf ball 1 comprises a core 2 and a cover 3, wherein either of core 2

or cover 3 incorporates at least one layer comprising a foamed or unfoamed metallocene blend.

Similarly, Fig. 2 illustrates a golf ball according to the invention incorporating a multi-piece core. Golf ball 5 10 comprises a cover 12, a core having a center 14 and at least one additional core layer 16. Any of the cover 12, center 14, or core layer 16 may incorporate at least one layer of a foamed or unfoamed metallocene blend.

Conventional materials useful in centers, cores, or 10 core layers of the golf balls of the invention include, but are not limited to, compositions having a base rubber, a crosslinking agent, and a filler. The base rubber typically includes natural or synthetic rubbers. A preferred base rubber is 1,4-polybutadiene having a cis-structure of at 15 least 40 %. Natural rubber, polyisoprene rubber and/or styrene-butadiene rubber may be optionally added to the 1,4-polybutadiene. Crosslinking agents include metal salts of unsaturated fatty acids, such as zinc or magnesium salts acrylic or methacrylic acid. The filler typically includes 20 materials such as zinc oxide, barium sulfate, silica, calcium carbonate, zinc carbonate and the like. Golf balls of the invention may also have conventional wound cores.

Golf balls of the invention may also include a mantle layer, preferably comprising a least one layer of a 25 foamed or unfoamed metallocene polymer blend, situated between the cover and the core. A golf ball incorporating a mantle layer is illustrated in Fig. 3, which depicts golf ball 20, having cover 23, core 24, and a mantle layer 25 situated between the cover and the core. Any of cover 23, 30 core 24, and mantle layer 25 may incorporate at least one layer of a foamed or unfoamed metallocene blend. Moreover, core 24 may be a one-piece core, a multi-layer core, or a wound core.

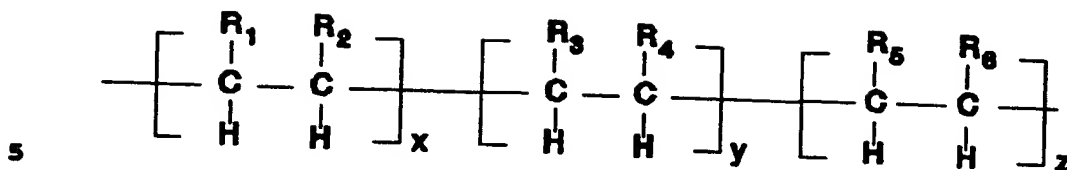
Golf balls according to the invention may 35 incorporate cover layers comprising foamed or unfoamed metallocene polymer blends or conventional materials, including balata and ionomer cover stock. Metallocene

polymer blend cover layers according to the invention may be used with conventional solid or wound cores, as well as those comprising metallocene polymer blends.

The narrow molecular weight distributions of
5 metallocene polymers provide more uniform compositions and improved tensile properties when compared to polyolefins polymerized with conventional catalysts. When a layer of foamed metallocene polymer blend is used in a golf ball cover or mantle, the ball has a softer feel than balls using hard a
10 ionomer, and is more deformable. The increased deformation of the cover and outer layers of the ball provides improved control due to the increased "bite" on the clubface when the ball is struck, which prevents or reduces sliding of the ball up the clubface, and allows more energy to be imparted
15 directly to the core at impact, providing a greater initial velocity. The improved control and feel are similar to those obtained using a soft balata cover without the decrease in durability that is typically associated with balata.

The use of foamed metallocene polymer also allows
20 the golf ball designer to adjust the density or mass distribution of the ball to adjust the angular moment of inertia, and, thus, the spin rate and performance of the ball. Foamed materials also offer a potential cost savings due to the reduced use of polymeric material.

25 Metallocene polymers useful in the golf balls of the invention are available commercially, and can be subjected to post-polymerization reactions to provide metallocene polymers with various pendant groups. Examples of metallocene polymers useful in the invention include, but
30 are not limited to homopolymers of ethylene and copolymers of ethylene and a second olefin, preferably, propylene, butene, hexene, octene, and norbornene. Generally, the invention includes golf balls having at least one layer comprising a blend that includes at least one metallocene polymer having
35 the formula:



wherein

R_1 is hydrogen, branched or straight chain alkyl
10 such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl,
and octyl, carbocyclic, aromatic or heterocyclic;

R_2 is hydrogen, lower alkyl including C_1-C_3 ,
carbocyclic, aromatic or heterocyclic

R_3 is hydrogen, lower alkyl including C_1-C_3 ,
15 carbocyclic, aromatic or heterocyclic;

R_4 is selected from the group consisting of H ,
 C_nH_{2n+1} , where $n = 1$ to 18 , and phenyl, in which from 0 to 5 H
within R_4 can be replaced by substituents selected from the
group consisting of $COOH$, SO_3H , NH_2 , F , Cl , Br , I , OH , SH ,
20 silicone, lower alkyl esters and lower alkyl ethers, with the
proviso that R_3 and R_4 can be combined to form a bicyclic
ring;

R_5 is hydrogen, lower alkyl including C_1-C_3 ,
carbocyclic, aromatic or heterocyclic;

25 R_6 is hydrogen, lower alkyl including C_1-C_3 ,
carbocyclic, aromatic or heterocyclic; and

wherein x , y and z are the relative percentages of
each co-monomer. The number x can range from $1-99$ percent or
more preferably from $10-70$ percent and most preferred, from
30 about $10-50$ percent. The number y can be from $99-1$ percent,
preferably, from $90-30$ percent, or most preferably, $90-50$
percent. The number z can range from 0 to 49 percent.

In the preferred metallocene copolymer, R_1 is
hydrogen or lower alkenyl, R_2 is hydrogen or alkyl, including
35

carbon chains having from 1 to 10 carbon atoms, R_3 is hydrogen or lower alkyl or alkenyl such as carbon chains having 1-10 carbon atoms, and R_4 is a lower alkyl group having from 1-10 carbon atoms. For terpolymers, where z is not zero, R_3 is preferably hydrogen or lower alkyl or alkenyl such as carbon chains having 1-10 carbon atoms, and R_4 is a lower alkyl group having from 1-10 carbon atoms. In the most preferred copolymer, R_1 and R_2 are hydrogen, R_3 is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, and R_4 is a straight carbon chain having 6 carbon atoms. For terpolymers, R_3 is most preferably hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, and R_4 is a straight carbon chain having 6 carbon atoms.

The subject metallocene copolymers can be random or block copolymers. Additionally, the subject metallocene polymers may be isotactic, syndotactic or atactic. The pendant groups creating the isotactic, syndotactic or atactic polymers are chosen to determine the interactions between the different polymer chains making up the resin to control the final properties of the resins used in golf ball covers.

As used herein, the phrase branched or straight chain alkyl means any substituted or unsubstituted acyclic carbon-containing compounds, including alkanes, alkenes and alkynes. Examples of alkyl groups include lower alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl or tert-butyl; upper alkyl, for example, octyl, nonyl, decyl, and the like; and lower alkylene, for example, ethylene, propylene, propyldiene, butylene, butyldiene, pentene, hexene, heptene, octene, norbornene, nonene, decene and the like. The ordinary skilled artisan is familiar with numerous linear and branched alkyl groups, which are within the scope of the present invention.

In addition, such alkyl groups may also contain various substituents in which one or more hydrogen atoms has

been replaced by a functional group. Functional groups include, but are not limited to hydroxyl, amino, carboxyl, sulfonic amide, ester, ether, phosphates, thiol, nitro, silane and halogen (fluorine, chlorine, bromine and iodine),
5 to mention but a few.

As used herein, substituted and unsubstituted carbocyclic means cyclic carbon-containing compounds, including, but not limited to cyclopentyl, cyclohexyl, cycloheptyl, adamantyl, and the like. Such cyclic groups may
10 also contain various substituents in which one or more hydrogen atoms has been replaced by a functional group. Such functional groups include those described above, and lower alkyl groups having from 1-28 carbon atoms. The cyclic groups of the invention may further comprise a heteroatom.
15 For example, in a specific embodiment, R_2 is cyclohexanol.

As used herein, substituted and unsubstituted aryl groups means a hydrocarbon ring bearing a system of conjugated double bonds, typically comprising $4n + 2 \pi$ (pi) ring electrons, where n is an integer. Examples of aryl
20 groups include, but are not limited to phenyl, naphthyl, anisyl, toluyyl, xylenyl and the like. According to the present invention, aryl also includes heteroaryl groups, e.g., pyrimidine or thiophene. These aryl groups may also be substituted with any number of a variety of functional
25 groups. In addition to the functional groups described above in connection with substituted alkyl groups and carbocyclic groups, functional groups on the aryl groups can include nitro groups.

As mentioned above, R_1 and R_2 can also represent any
30 combination of alkyl, carbocyclic or aryl groups, for example, 1-cyclohexylpropyl, benzyl cyclohexylmethyl, 2-cyclohexylpropyl, 2,2-methylcyclohexylpropyl, 2,2-methylphenylpropyl, 2,2-methylphenylbutyl.

The metallocene copolymers useful in the present
35 invention are commercially available under the trade name

AFFINITY® polyolefin plastomers and ENGAGE® polyolefin elastomers by Dow Plastics Company. Other commercially available metallocene polymers can be used such as Exxon's Exact® and Dow's Insight® line of resins which have superior flexibility and clarity, as well as toughness. The Exact® and Insight® line of polymers also have novel rheological behavior in addition to their other properties as a result of using a metallocene catalyst technology. Metallocene polymers are also available from Sentinel Products Corporation of Hyannis, Massachusetts, as foamed sheets for compression molding and in unfoamed pelletized form suitable for injection molding. The foamed metallocene polymers sheets are available in thicknesses ranging from about 0.027 to 0.625 inches (0.069 to 0.159 cm). Closed cell bun stock is also available in thicknesses of up to 4 inches (10.2 cm).

The metallocene polymer blend golf ball compositions of the present invention comprise compatible blends of at least one metallocene polymer and at least one ionomer that are formed using blending methods well known in the art. In particular, the metallocene polymer blends comprise compatible blends of metallocene polymers and ionomers, such as ethylene methacrylic acid ionomers, and ethylene acrylic acid ionomers, and their terpolymers, sold commercially under the trade names SURLYN® and IOTEK® by DuPont and Exxon respectively. The metallocene polymer blends useful in the golf balls of the invention can also include other polymers, such as poly(ethylethylene), poly(heptylethylene), poly(hexyldecylethylene), poly(isopentylethylene), poly(1,1-dimethyltrimethylene), poly(1,1,2-trimethyltrimethylene), poly(butyl acrylate), poly(4-cyanobutyl acrylate), poly(2-ethylbutyl acrylate), poly(heptyl acrylate), poly(2-methylbutyl acrylate), poly(3-methylbutyl acrylate), poly(N-octadecylacrylamide), poly(octadecyl methacrylate), poly(butoxyethylene), poly[1,1-bis(trifluoromethoxy)difluoroethylene],

poly(methoxyethylene), poly(pentyloxyethylene),
poly(1,1-dichloroethylene), poly(cyclopentylacetoxymethylene),
poly(4-[(2-butoxyethoxy)methyl]styrene),
poly(4-dodecylstyrene), poly(4-tetradecylstyrene),
5 poly(phenethylmethylethylene),
poly[oxy(allyloxymethyl)ethylene],
poly[oxy(ethoxymethyl)ethylene], poly(oxyethylethylene),
poly(oxytetramethylene), poly(oxytrimethylene),
poly(oxycarbonylpentamethylene), poly(oxycarbonyl-3-
10 methylpentamethylene), poly(oxycarbonyl-1,5-
dimethylpentamethylene), poly(oxy-2,2,3,3,4,4-
hexafluoropentamethyleneoxyadipoyl), poly[oxy(methyl)-3,3,3-
trifluoropropylsilylene-3p3-difluoropentamethylene(methyl)-
3,3,3-trifluoropropylsilylene], poly(silanes) and
15 poly(silazanes), main-chain heterocyclic polymers and
poly(furan tetracarboxylic acid diimides) as well as the
classes of polymers to which they belong.

The preferred golf ball compositions comprise one
or more ionomer resins having a flexural modulus of from
20 about 50 psi to about 150,000 psi and a metallocene copolymer
of an olefin having a flexural modulus of from about 500 psi
to 200,000 psi. In a most preferred embodiment of the
present invention EXACT® 4033 is combined with IOTEK® 7030 or
SURLYN® 7940 to form combination blends suitable for use in
25 golf ball centers and cover, core, and mantle layers.

The amounts of polymers used in the golf ball
compositions of the invention can vary from 1 to 100 phr of
the metallocene polymers to 99 to 0 phr of other polymers or
ionomers, preferably, 95 to 5 phr metallocene polymers and 5
30 to 95 phr ionomer or other polymer. Most preferred is from
about 95 to 30 phr metallocene polymer and from about 5 to 70
phr of other polymer or ionomer.

Further compositions may also be added to the
compatible blends of the invention, such as, for example,

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coloring agents, reaction enhancers, crosslinking agents, dyes, lubricants, fillers, excipients, process aids and other compounds commonly added to polymeric materials and/or golf ball covers.

5 The present invention relates to golf balls of any size. While USGA specifications limit the size of a competition golf ball to more than 1.68 inches (4.27 cm) in diameter, golf balls of any size can be used for leisure golf play. The preferred diameter of the golf balls is from about
10 1.68 inches to about 1.8 inches (4.57 cm). The more preferred diameter is from about 1.68 inches to about 1.76 inches (4.47 cm). A diameter of from about 1.68 inches to about 1.74 inches (4.42 cm) is most preferred, however diameters anywhere in the range of from 1.7 to about 1.95
15 inches (4.3 to 4.95 cm) can be used. Oversize golf balls above about 1.76 inches to golf balls having diameters as big 2.75 inches (7 cm) are also within the scope of the present invention.

 Metallocene polymer blend layers may be produced in
20 golf balls in accordance with the present invention by injection molding or compression molding a layer of metallocene polymer blend material about a previously formed center or core, cover, or mantle layer. Cores comprising a metallocene polymer blend may also be formed directly by
25 injection molding or compression molding. When the layer or core is injection molded, a physical or chemical blowing or foaming agent may be included to produce a foamed layer. Blowing or foaming agents useful in forming foamed metallocene polymer blends include, but are not limited to
30 organic blowing agents, such as azobisformamide; azobisisobutyronitrile; diazoaminobenzene; N,N-dimethyl-N,N-dinitroso terephthalamide; N,N-dinitrosopentamethylene-tetramine; benzenesulfonyl-hydrazide; benzene-1,3-disulfonyl hydrazide;
35 diphenylsulfon-3-3, disulfonyl hydrazide; 4,4'-oxybis benzene sulfonyl hydrazide; p-toluene sulfonyl semicarbazide; barium azodicarboxylate; butylamine nitrile; nitroureas;

trihydrazino triazine; phenyl-methyl-uranthan;
p-sulfonhydrazide; peroxides; and inorganic blowing agents
such as ammonium bicarbonate and sodium bicarbonate. A gas,
such as air, nitrogen, carbon dioxide, etc., can also be
5 injected into the blend during the injection molding process.

In a further embodiment, foamed metallocene polymer
blends may be formed by blending microspheres with the
metallocene polymer blend either during or before the molding
process. Polymeric, ceramic, metal, and glass microspheres
10 are useful in the invention, and may be solid or hollow and
filled or unfilled. Microspheres up to about 1000
micrometers in diameter are useful in the metallocene polymer
blends of the invention.

For compression molded metallocene polymer blend
15 layers, half-shells made by injection molding a metallocene
polymer blend in a conventional half-shell mold or by
compression molding commercially available sheets of foamed
metallocene are used. The half-shells are placed about a
previously formed center or core, cover, or mantle layer, and
20 the assembly is introduced into a compression molding
machine, and compression molded at about 250 to 400°F. The
molded balls are then cooled while still in the mold, and
finally removed when the layer of metallocene polymer blend
is hard enough to be handled without deforming. Additional
25 core, mantle, and cover layers are then molded onto the
previously molded layers, as needed, until a complete ball is
formed.

After the final cover layer of the ball has been
molded, the ball undergoes various conventional finishing
30 operations such as buffing, painting and stamping.

Blending of the metallocene polymer and ionomer
resins is accomplished in a conventional manner using
conventional equipment. Good results have been obtained by
mixing the metallocene polymer and ionomer resins in a solid,
35 pelletized form and then placing the mix into a hopper which
is used to feed the heated barrel of the injection molding
machine. Further mixing is accomplished by a screw in the

heated barrel. The injection molding machine is used either to make preformed half-shells for compression molding or for molding flowable metallocene polymer blend using a retractable-pin mold. Such machines are conventional.

5 These and other aspects of the present invention may be more fully understood by reference to the following examples.

While these examples are meant to be illustrative of golf balls made according to the present invention, the present invention is not meant to be limited by the following examples. All parts are by weight unless otherwise specified.

Formulations containing the components IOTEK® 7030 (a copolymer of ethylene and acrylic acid neutralized by zinc oxide) with EXACT® 4033 (a metallocene copolymer of ethylene with 1-butene) and the compatibilizer ATX 320® were developed according to the present invention.

Table I summarizes the physical properties of these components used in the blends.

20 Table I: Physical properties of various components used in the blends

Property	Iotek 7030	Escor ATX 320	Exact 4033	Sartyn 7940	Sartyn R320
25 Hardness (Shore-D or A)	55D	83 A	85 A	68 D	84 A
Tensile Strength, psi	3500	1800	3000	3800	3100
Tensile strain at break, %	395	>800	620	285	770
Tensile modulus, psi	NA	1300	720 @300% strain	NA	NA
30 Flexural modulus, psi	16,000	3700	3300	61000	2800

Tensile and flexural test samples are produced by injection molding of the formulations by following a standard operating procedure. The test samples are annealed in an air circulating oven at 140°F for 24 hours, followed by conditioning at room temperature for seven days before

testing. Both tensile and flexural measurements were carried out by following ASTM D638 and D790 procedures, respectively.

Golf ball covers are produced by injection molding by following a routine molding procedure. Cores or mantle layers and cores measuring about 1.4 to 1.58 inch (3.5 to 4 cm) diameter are used to make golf balls by compression molding of the cover composition about the core or mantle layer and core.

After completion of the ball molding process, the balls are buffed, sand blasted and painted for evaluation. Hardness, PGA compression, spin, velocity, shear resistance, durability using a dual pendulum, ink and paint durability tests are performed on the finished balls. These results are shown in Table III.

The tensile, flexural, hardness and flow properties of the blends based on IOTEK® 7030 and EXACT® 4033 are summarized in Table II. Properties from blends 1 and 2 were used as a control. Although Shore-D hardness and tensile modulus decreases as EXACT® 4033 level increases for blend 5, tensile strength surprisingly was much higher than for blends 2 through 4. Also, a significant increase in the percent strain at break value was obtained for blend 5.

Blends of polymers including EXACT® 4033 and IOTEK® 7030 ionomer, exhibit excellent properties when used in golf ball covers which is unexpected since EXACT® 4033 material is hydrophobic whereas IOTEK® 7030 is hydrophilic. Although Shore-D hardness decreases with increases in EXACT® 4033 level in the blends, surprisingly both initial velocity and coefficient of restitution (COR) remain constant for blends 3 through 5. See Table III. These results are unusual since initial velocity tends to decrease as hardness decreases.

Table II: Comparison of various physical properties of blends based on Iotek® 7030® with Exact® 4033.

Ingredients	Blend				
	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5
Iotek 7030	100	90	80	70	50
ATX 320	-	10	10	10	10
Exact 4033	-	-	10	20	40
White concentrate	5	5	5	5	5
Physical Properties					
Hardness (Shore-D)	58	56	60	50	45
Tensile strength at break, psi	2701	2453	2174	2383	2899
Tensile strain at break, %	393	441	412	556	875
Tensile modulus, kpsi	17.7	15.3	14.4	12.2	7.4
Flexural modulus, kpsi	36.2	32.3	29.9	26.4	21.7
Melt flow index at 185° C, g/10min	5.3	6.2	5.5	4.3	3.1

Note: Tensile properties were measured from the ball covers.

In general, in the golf ball art, durability decreases as the non-ionic olefin component increases in an ionomer blend. Also, as mentioned above, durability of blends of ionomers with a homopolymer such as polyethylene is poor (failed after 5 to 10 hits) due to incompatibility of these components. However, the present invention unexpectedly shows that it is possible to obtain improved durability for golf ball cover compositions containing EXACT® 4033 in various compositions.

A significant increase in the spin rate from the driver and 5-iron was obtained for balls which contain blends of metallocene polymer and ionomers in the cover compositions.

Table III: Comparison of various golf ball properties of blends based on Iotek 7030[®] with Exact[®] 4033.

5	Physical and Ball Properties	Blend 1	Blend 2	Blend 3	Blend 4	Blend 5
	Hardness (Shore-D)	65	60	60	57	55
	PGA compression	104	103	102	101	100
	Spin rate from the driver, rpm	3264	3254	3404	3526	3885
	Spin rate from the 5-iron, rpm	7653	7807	8100	8197	9103
10	Initial velocity, ft/s	252.7	252.7	252.6	252.6	252.7
	Coefficient of restitution	0.802	0.801	0.799	0.804	0.800
	Durability at room temperature, # hits to 50% failure	150	400	200	250	400

15 More recently, a study was initiated to displace the low modulus Surlyn[®] 8320 ionomer by EXACT[®] 4033 in the blend formulations as described in Table IV; a blend 8 containing 9.5 wt percent of ATX 320[®] was included in this study in order to find out whether the ATX 320[®] is necessary to achieve acceptable mechanical and ball properties.

20 Tensile strength and percent strain at break increases for blends containing the EXACT[®] 4033 yet still has a higher tensile modulus than the low modulus SURLYN[®] 8320 blend as indicated in Table IV. This behavior is unexpected.

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**Table IV: Comparison of
various physical properties of
cover blends based on
Surlyn 7940^R with Surlyn^R 8320 and Exact^R 4033**

5	Ingredients	Blend 6	Blend 7	Blend 8
	Surlyn 7940	55	55	50
	Surlyn 8320	45	-	-
	Exact 4033	-	45	40
10	ATX 320	-	-	10
	White concentrate	5	5	5
	Physical Properties			
15	Tensile strength at break*, psi	2792	3425	3455
	Tensile strain at break*, %	570	777	763
	Tensile modulus *, kpsi	14.2	13.1	13.3

20

Note: *Tensile properties were measured from the ball covers instead of molded specimens.

25

A significant increase in the spin rate from the driver is indicated for the blends containing EXACT® 4033 in comparison to a blend containing the low modulus SURLYN® 8320 (see Table V).

30

Further, initial velocity and coefficient of restitution results were found to be slightly better for blends containing an ionomer and an ethylene polymer such as those containing the EXACT® 4033 component than the low modulus SURLYN® 8320 component.

**Table V: Comparison of
various golf ball properties of
blends based on Surlyn 7940[®]
with Surlyn[®] 8320 and Exact[®] 4033**

5	<i>Physical and Ball Properties</i>	<i>Blend 6</i>	<i>Blend 7</i>	<i>Blend 8</i>
	Hardness (Shore-D)	60	60	57
	PGA compression	105	105	105
10	Spin rate from the driver, rpm	3526	3871	3896
	Spin rate from the 5-iron, rpm	7974	8623	8568
	Initial velocity, ft/sec	252.3	253.0	252.8
	Coefficient of restitution	0.804	0.807	0.808
	Durability at room temperature, # hits	400	400	400
15	Number of balls failed after durability test	none	none	none

It appears from the above study that the presence of ATX 320[®] did not contribute to further improvements in the ball properties.

In comparing balls with covers made from 52.4 weight percent Surlyn 7940/42.9 weight percent Surlyn 8320 to balls with covers in which the Surlyn 8320 was replaced by Exact 4033 or by Exact 4033 with Fusabond MB-110D, 226D or 280D, the balls with Exact 4033 had both a higher spin rate and better durability, as shown in Table VI. Thus, the 52.4 weight percent Surlyn 7940/42.9 weight percent Surlyn 8320 had a spin rate of 3362 rpm when hit by a driver/8657 rpm when hit by an 8-iron, while the 52.4 weight percent Surlyn 7940/42.9 weight percent Exact 4033 had corresponding spin rates of 3619 and 9150 rpm. In the hit test at room temperature, cracking was observed after 650 hits for the Surlyn 7940/Surlyn 8320 blend, but only after 1000 hits for the Surlyn 7940/Exact 4033 blend.

Table VI: Comparison of Golf Ball Properties For
Blends of Surlyn 7940, Surlyn 8320
with Exact 4033, FUSADOND Polymers

I. Ingredients	EP	#10	#11	#12	#13
Surlyn 7940 (15% Acid Ionomer-Li)	55	55	55.0	55.0	55.0
Surlyn 8320 (15% Acid Ionomer-Na)	45	-	-	-	-
Exact 4033	-	45	45.0	45.0	45.0
Fusabond MB-110D (Ethylene - 0.9 wt. % maleic anhydride melt flow index 30)	-	-	10.0	-	-
Fusabond MB-226D (Ethylene - 0.9 wt. % maleic anhydride melt flow index 1.5)	-	-	-	10.0	-
Fusabond MB-280D (EPDM with 2% maleic anhydride m.L.S.O)	-	-	-	-	10.0
White Concentrate	5.0	5.0	5.0	5.0	5.0
II. Performance					
Hit Test at RT (50% fail)	650	1000	over 1000	over 1000	over 1000
Cold Crack Test at 5°F	No fail	No fail	No fail	No fail	No fail
Spin Rate from Driver (rpm)	3362	3619	3408	3436	3599
Spin Rate from 8 - Iron (rpm)	8657	9150	8770	8753	9078

The information in Table VII establishes that low modulus Surlyn materials can be replaced by polymers discussed herein with little change in spin rate.

Table VII: Comparison of Golf Ball Properties
Of Surlyn® Blends
With Affinity® PF 1140

Ingredients	Surlyn 7940	Surlyn 8320	Affinity PF1140	White Concentrate	Spin Rate Driver (rpm)	Flex Modules
A#1	92.5	7.5		5	3216	62.2 ± 1.67
A#2	92.5	3.75	3.75	5	3304	55.9 ± 1.20
A#3	85	15	—	5	3348	54.8 ± 1.70
A#4	85	10	5	5	3221	56.4 ± 2.80
A#5	85	7.5	7.5	5	3307	57.2 ± 2.60
A#6	77.5	22.5	—	5	3281	46.8 ± 2.80
A#7	77.5	15.0	7.5	5	3317	50.8 ± 1.40
A#8	77.5	11.25	11.25	5	3346	48.7 ± 2.1
A#9	55	45	—	5	3489	27.1 ± 2.2
A#10	55	37.5	7.5	5	3421	24.6 ± 1.8
A#11	55	30	15	5	3607	22.7 ± 2.9
A#12	55	22.5	22.5	5	3497	23.4 ± 2.4
A#13	95	—	5	5	3146	64.2 ± 3.4
A#14	90	—	10	5	3288	68.1 ± 2.6

While it is apparent that the invention disclosed herein is well calculated to fulfill the objects stated above, it will be appreciated that numerous modifications and embodiments may be devised by those skilled in the art. Therefore, it is intended that the appended claims cover all such modifications and embodiments as falling within the true spirit and scope of the present invention.

CLAIMS

We claim:

1. A golf ball having least one layer, the layer formed of a metallocene polymer blend, comprising from about 5 1 to about 100 phr of at least one metallocene polymer and from about 99 to 0 phr of at least one ionomer.
2. The golf ball according to claim 1, comprising a cover, wherein the layer forms at least a portion of the 10 cover.
3. The golf ball according to claim 2, wherein the layer has a foamed structure.
- 15 4. The golf ball according to claim 2, wherein the layer has a Shore D hardness of from about 15 to about 80.
5. The golf ball according to claim 2, wherein the layer has a thickness of from about 0.005 to about 0.125 20 inch.
6. The golf ball according to claim 1, comprising a core, wherein the layer forms at least a portion of the core.
- 25 7. The golf ball according to claim 6, wherein the core comprises a liquid center.
8. The golf ball according to claim 6, wherein the 30 layer has a foamed structure.
9. The golf ball according to claim 6, wherein the layer has a Shore D hardness of from about 15 to about 80.

35

10. The golf ball according to claim 6, wherein the core has a diameter of from about 1.0 to about 1.63 inch, and the layer has a thickness of from about 0.005 to about 0.125 inch.

5

11. The golf ball according to claim 1, further comprising a cover and a core and a mantle situated between the cover and the core.

10

12. The golf ball according to claim 11, wherein the core comprises a liquid or solid center wrapped in elastomeric windings.

13. The golf ball according to claim 11, wherein the layer forms at least a portion of the mantle.

14. The golf ball according to claim 13, wherein the core has a diameter of from about 1 to about 1.63 inch, the cover has a thickness of from about 0.005 to about 0.125 inch, and the mantle has a thickness of from about 0.005 to about 0.125 inch.

15. The golf ball according to claim 13, wherein the layer has a foamed structure.

25

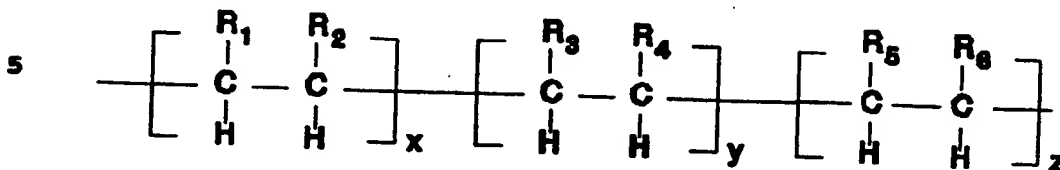
16. The golf ball according to claim 13, wherein the layer has a Shore D hardness of from about 15 to about 80.

30

17. The golf ball according to claim 1, wherein the metallocene polymer is chosen from the group consisting of polyethylene and copolymers of ethylene with butene, hexene, octene, and norbornene.

35

18. The golf ball according to claim 1, wherein the metallocene polymer is of the formula:



wherein

10 R_1 is hydrogen;

R_2 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

R_3 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

15 R_4 is selected from the group consisting of H, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , C_9H_{19} , $C_{10}H_{21}$, and phenyl, in which from 0 to 5 H within R_4 can be replaced by substituents selected from the group consisting of $COOH$, SO_3H , NH_2 , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl
20 ethers, with the proviso that R_3 and R_4 can be combined to form a bicyclic ring;

R_5 is hydrogen, lower alkyl including C_1 - C_3 , carbocyclic, aromatic or heterocyclic;

25 R_6 is hydrogen, lower alkyl including C_1 - C_3 , carbocyclic, aromatic or heterocyclic; and

wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer and z ranges from 0 to 49 weight per cent of the polymer.

30 19. The golf ball according to claim 1, wherein the metallocene polymer has a flexural modulus of from about 500 psi to 200,000 psi, and the ionomer has a flexural modulus of from about 50 psi to about 150,000 psi.

35

20. The golf ball according to claim 1, wherein the metallocene polymer blend has a foamed structure, and, further wherein the metallocene polymer blend has a flexural modulus of from about 1000 to about 150,000 psi.

5

21. The golf ball according to claim 1, further comprising a cover and a core, wherein the metallocene polymer blend has a foamed structure.

10

22. The golf ball according to claim 21, wherein the layer forms at least a portion of the core, and the cover comprises a density increasing filler material.

23. The golf ball according to claim 21, wherein 15 the layer forms at least a portion of the cover, and the core comprises a density increasing filler material.

24. The golf ball according to claim 21, further comprising a mantle situated between the cover and the core, 20 wherein the layer forms at least a portion of the mantle, and either the cover or the core comprises a density increasing filler material.

25. A golf ball comprising a cover and a core and 25 a mantle situated between the cover and the core, wherein at least one of the cover, the core, and the mantle comprises at least one layer, the layer formed of a metallocene polymer blend, comprising from about 1 to about 100 phr of at least one metallocene polymer and from about 99 to 0 phr of at 30 least one ionomer.

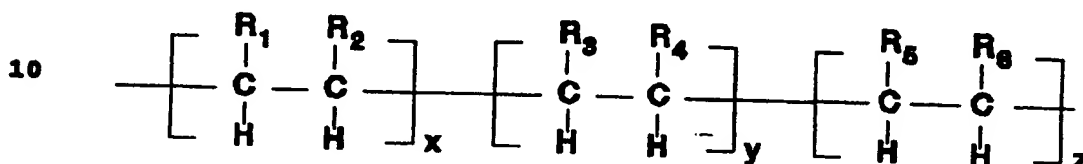
26. The golf ball according to claim 25, wherein the layer has a foamed structure.

35

27. The golf ball according to claim 25, wherein the metallocene polymer is chosen from the group consisting of copolymers of ethylene with butene, hexene, octene, and norbornene.

5

28. The golf ball according to claim 25, wherein the metallocene polymer is of the formula:



15 wherein

R_1 is hydrogen;

R_2 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

20 R_3 is hydrogen or lower alkyl selected from the group consisting of CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , and C_5H_{11} ;

R_4 is selected from the group consisting of H, CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , C_5H_{11} , C_6H_{13} , C_7H_{15} , C_8H_{17} , C_9H_{19} , $\text{C}_{10}\text{H}_{21}$, and phenyl, in which from 0 to 5 H within R_4 can be replaced by substituents selected from the group consisting of COOH , SO_3H , NH_2 , F, Cl, Br, I, OH, SH, silicone, lower alkyl esters and lower alkyl ethers, with the proviso that R_3 and R_4 can be combined to form a bicyclic ring;

25 R_5 is hydrogen, lower alkyl including $\text{C}_1\text{-C}_3$, carbocyclic, aromatic or heterocyclic;

30 R_6 is hydrogen, lower alkyl including $\text{C}_1\text{-C}_3$, carbocyclic, aromatic or heterocyclic; and

wherein x ranges from 99 to 50 weight per cent of the polymer, y ranges from 1 to 50 weight per cent of the polymer and z ranges from 0 to 49 weight per cent of the polymer.

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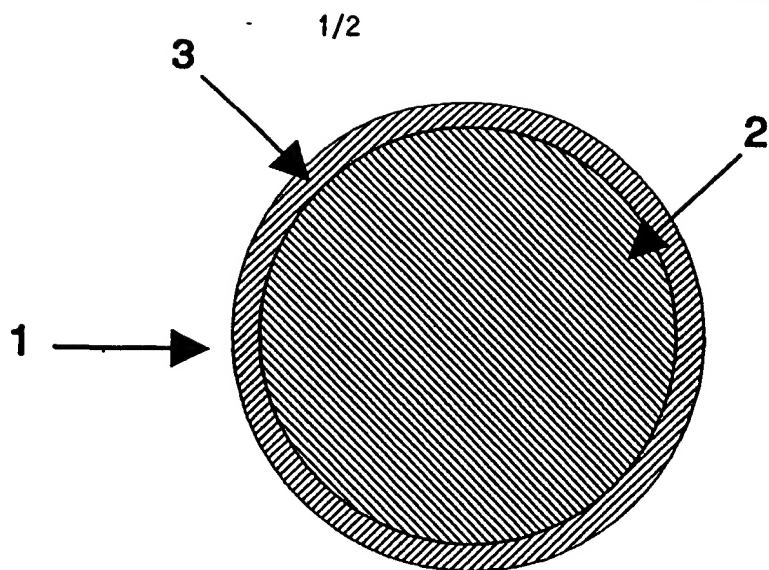


FIGURE 1

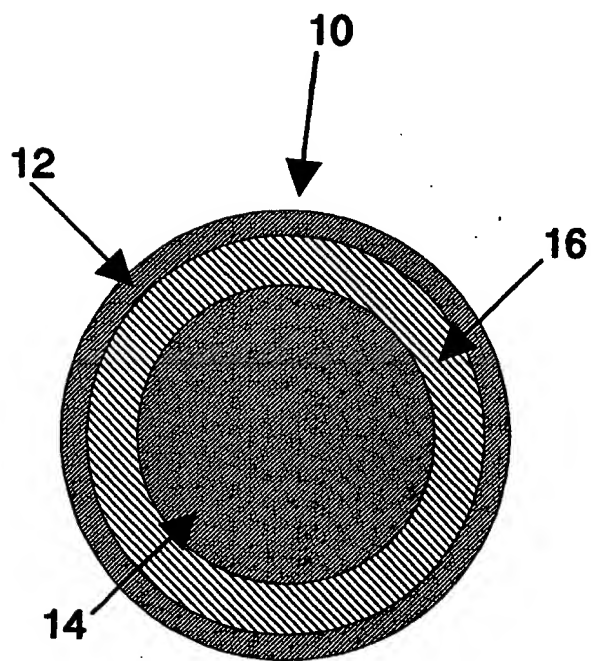


FIGURE 2

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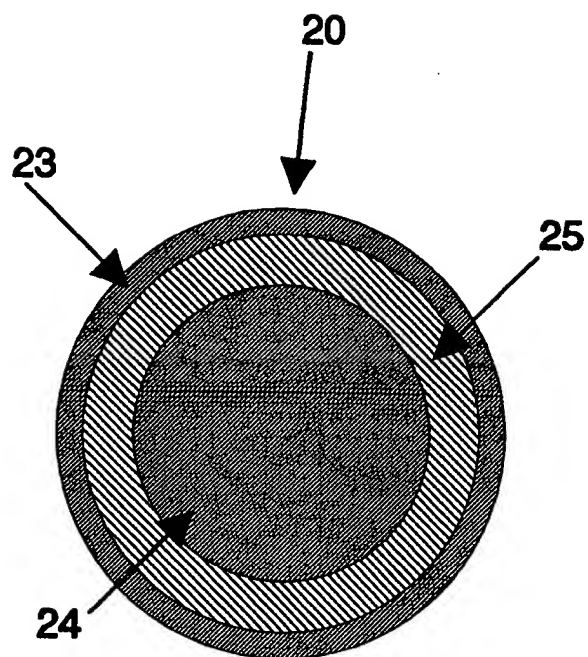


FIGURE 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/08775**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :A63B 37/08, 37/12; B32B 27/02

US CL :473/377, 371, 374; 428/515, 407

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 473/377, 371, 374; 428/515, 407; 524/908

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,572,722 A (HARRISON ET AL) 30 March 1971, columns 2-4.	1-28
Y	US 5,321,089 A (CADORNIGA ET AL) 14 June 1994, columns 2-4 and examples.	1-28
Y	US 5,397,840 A (SULLIVAN ET AL) 14 March 1995, columns 2-7.	1-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A document defining the general state of the art which is not considered to be of particular relevance	* X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E earlier document published on or after the international filing date	* Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & document member of the same patent family
* O document referring to an oral disclosure, use, exhibition or other means	
* P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

03 SEPTEMBER 1996

Date of mailing of the international search report

17 SEP 1996

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